14

THE EMISSION SPECTRUM OF ZnBr IN THE VISIBLE REGION

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(Plate 5)

ABSTRACT. The visible spectrum of ZnBr was reinvestigated in emission in the high frequency discharge. A system of bands degraded to red, designated as $B^2\Sigma - X^2\Sigma$ and occurring in the region $\lambda 4550 - \lambda 3600$ has been photographed with a medium quartz and plane grating spectrograph having a dispersion of 7 A°/mm. The vibrational constants derived in the analysis of this system are :

$$\omega'_e = 135.80 \text{ cm}^{-1}, \qquad \omega''_e = 269.80 \text{ cm}^{-1},$$

$$\omega'_e x'_e = 0.40 \text{ cm}^{-1}, \text{ and } \quad \omega''_e x''_e = 1.54 \text{ cm}^{-1}.$$

INTRODUCTION

The band spectrum of ZnBr was first reported in emission by Wieland (1929) in the region $\lambda 8470 - \lambda 3300$. The bands are degraded to the red and lie on a continuum with pronounced intensity maximum at $\lambda 8300$. The measurements of about thirty band heads in the region $\lambda 4500 - \lambda 3600$, which are weak in intensity and a general continuum covering them up, have been reported by Ramasastry *et al* (1950) but no analysis has been presented so far. The ultra violet bands of zinc bromide were known from the absorption study of Walter *et al* (1929). Howell (1943) examined these absorption bands and suggested a vibrational frequency of 220 cm^{-1} for the lower state. However, he himself doubted the data attributed to ZnBr molecule as the lower state frequency obtained is very nearly equal to the well established ground state frequency of 223.4 cm^{-1} for the ZnI molecule. Ramasastry *et al* (1950) obtained the red degraded ultra violet bands in emission and have analysed them into two component systems *C* and *D* of $^2\Pi \rightarrow {}^2\Sigma$ electronic transition with a $^2\Pi$ separation of 386 cm^{-1}. They suggested 312 cm^{-1} and 318 cm^{-1} as the lower state frequencies for the two systems. In view of the inconsistency in the above reported values for the vibrational constants of the ground state of this molecule it was felt necessary to analyse the bands in the visible region, and the present investigation was taken up. The results obtained are described here.

EXPERIMENTAL

The spectrum of ZnBr was excited in a high frequency discharge from a 125 Watt oscillator working in the frequency range 10-15 Mc/Sec., using a pure sample of zinc bromide in a pyrex discharge tube of conventional type. Continuous evacuation of the tube with a high vacuum pump and strong heating with a burner were necessary to maintain a characteristic white colour of the discharge. This condition was found to be most suitable and for preliminary survey the spectra were photographed on a Hilger medium quartz spectrograph. The final spectrograms were taken on a plane grating spectrograph with a dispersion of 7 Å/mm in the first order. Exposures of about 45 minutes were found to be sufficient for obtaining satisfactory spectrograms using Ilford N40 process plates. Measurements of band heads were made on a comparator using iron arc lines as standard.

RESULTS

The band spectrum of ZnBr recorded on a medium quartz spectrograph has been reproduced in fig. 1(a) which clearly reveals the nature and extent of the spectrum. The plane grating spectrogram has been reproduced in fig. 1(b) as it appears on the photographic plate to bring out the finer details of the spectrum. The bands are degraded to red and line-like structure is observed in the region $\lambda 3850 - \lambda 3750$ The wave lengths of the bands of $ZnBr^{79}$ along with their wavenumbers in vacuum, their visually estimated intensities and the assignment of the vibrational quantum numbers have been given in table 1. The measurements of the band heads reported by Ramasastry *et al* (1950) are given in column 3 of the table for comparison. In column 6 are included the differences between the observed and calculated values of the wave numbers of the band heads.

DISCUSSION

The bands obtained in the present investigation are with fairly good definition and clarity and in addition to the thirty bands reported earlier sixty-nine more bands have been measured. It was observed that the bands in the region $\lambda 3900 - \lambda 3750$ were most intense and their intensities on either side decrease slowly. For most of the halides of this group of the periodic table it has been observed that the intensity distribution follows an open Condon parabola. It is therefore suggestive that the bands in the region may form the apex of the parabola. Careful measurements of the bands in this region revealed that a decreasing separation ranging from 270 cm^{-1} to 255 cm^{-1} amongst the alternate members of this group exists. The progressions marked in fig. 1(b) were first selected on this basis and a systematic analysis was then followed up.

The appearance of the bands in the region $\lambda 3900 - \lambda 3750$ is misleading as it shows partial resolution of rotational structure. The following reasons, however, lead us to believe that it should be treated as vibrational structure only.

Indian Journal of Physics
Vol 42 No. 2
PLATE - 5

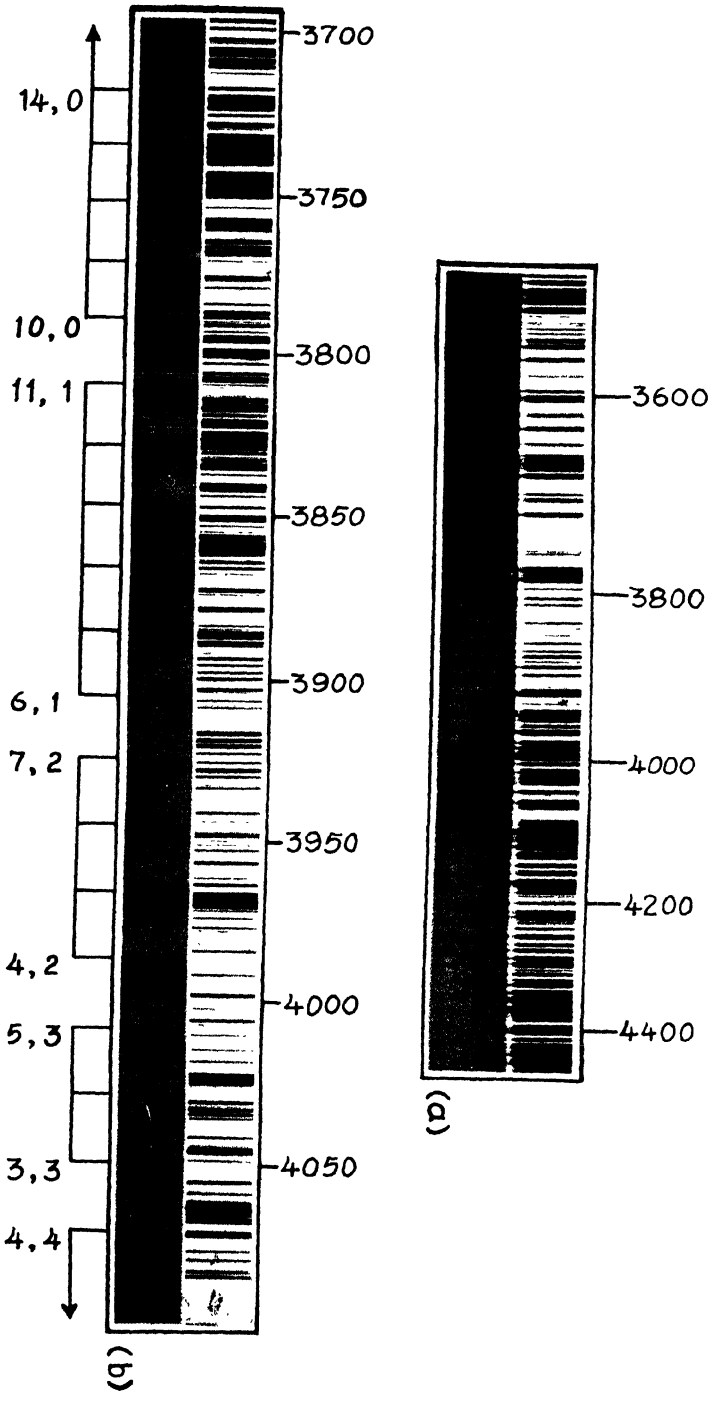

Fig. 1 (a) The medium quartz spectrogram of ZnBr molecule in the visible region. (b) Spectrogram (negative) taken on a Carl - Zeiss plane grating pectrograph.

Table 1

Wave lengths, wave numbers, intensity and vibrational assignments for the bands of $ZnBr^{79}$

Wave length in Å	Wave number in cm^{-1}	Values of Ramasastry *et al*	Intensity	Assignment (v', v'')	$\nu_{obs.} - \nu_{cal.}$
4227.5	23648	23634	6	1,6	−5
4206.0	23769	23780	6	0,5	0
4182.2	23904	23908	6	1,5	0
4161.3	24024	24029	6	0,4	0
4158.9	24038		6	2,5	0
4138.0	24159	24148	6	1,4	0
4117.3	24281	24280	6	0,3	0
4114.9	24295		6	2,4	2
4094.4	24417		6	1,3	1
4093.3	24423	24422	6	3,4	−3
4072.1	24550		5	2,3	0
4070.7	24559	24560	6	4,4	0
4049.9	24685	24691	7	3,3	1
4028.5	24816	24819	7	4,3	0
4007.2	24948	24956	7	5,3	0
3986.5	25077	25068	8	4,2	0
3984.4	25091		3	20, 10	0
3966.0	25207	25207	8	5,2	−2
3946.6	25331		3	20,9	1
3945.4	25339	24338	8	6,2	−1
3927.7	25453		3	19,8	0
3926.3	25462		6	13,5	0
3925.4	25468	25477	7	7,2	−2
3910.2	25567		3	22,9	−1
3909.5	25571		3	20,8	−1
3908.3	25579		4	18,7	2
3907.3	25586		5	14,5	0
3906.2	25593		6	12,4	2
3905.3	25599		7	8,2	0
3904.5	25604	25608	8	6,1	1
3893.4	25677		2	25,10	−1
3892.4	25684		3	23,9	−1
3890.3	25698		3	19,7	0
3889.3	25704		5	17,6	0
3887.5	25716		6	13,4	0
3886.6	25722		7	11,3	0
3885.4	25730	25729	8	7,1	−3
3874.9	25800		2	24,9	−2
3873.5	25809		3	22,8	−1
3871.1	25825		4	18,6	0
3869.9	25833		4	16,5	0
3868.7	25841		6	14,4	0
3867.5	25849		7	12,3	1
3866.6	25855		8	10,2	−1

Table 1 (*Contd.*)

Wave length in Å	Wave number in cm^{-1}	Values of Ramasastry *et al*	Intensity	Assignment (v', v'')	$\nu_{obs.} - \nu_{cal.}$
3865.2	25865	25866	9	8,1	2
3864.1	25872		5	6,0	2
3857.3	25918		4	25,9	0
3856.2	25925		3	23,8	−2
3854.7	25935		3	21,7	−2
3853.3	25945		3	19,6	−1
3850.3	25965		6	15,4	0
3848.9	25974		7	13,3	0
3848.0	25980		9	11,2	−3
3846.1	25993	25990	9	9,1	1
3845.1	26000		6	7 0	0
3838.6	26044		3	24,8	0
3837.1	26054		3	22,7	−1
3835.6	26064		3	20,6	−2
3833.4	26079		4	18,5	2
3831.9	26089		5	16,4	1
3827.7	26118		10	10,1	−1
3825.9	26130	26130	9	8,0	0
3821.4	26161		6	25,8	1
3819.3	26175		4	23,7	3
3816.1	26197		4	19,5	0
3814.3	26210		5	17,4	0
3812.8	26220		6	15,3	−2
3810.4	26236		7	13,2	1
3809.0	26246		10	11,1	0
3807.3	26258	26257	9	9,0	0
3804.5	26277		6	26,8	2
3802.6	26290		5	24,7	1
3800.9	26302		4	22,6	−1
3798.5	26319		4	20,5	2
3797.0	26329		5	18,4	−2
3794.7	26345		5	16,3	0
3792.9	26358		8	14,2	−1
3791.0	26371		9	12,1	−1
3788.9	26385	26385	9	10,0	−1
3781.6	26436		4	21,5	0
3779.4	26452		5	19,4	0
3776.9	26469		6	17,3	2
3774.8	26484		6	15,2	1
3772.8	26498		8	13,1	0
3770.7	26513	26511	8	11,0	0
3764.7	26555		3	22,5	1
3757.5	26606		6	16,2	0
3755.2	26622		7	14,1	0
3752.5	26641	26641	7	12,0	2
3745.4	26692		3	21,4	1
3743.0	26708		4	19,3	−1
3737.8	26746		4	15,1	0

Table 1 (*Contd.*)

Wave length in Å	Wave number in cm^{-1}	Values of Ramasastry *et al*	Intensity	Assignment (v', v'')	$\nu_{obs.}-\nu_{cal.}$
3735.0	26766	26766	7	13,0	1
3723.5	26849		5	18,2	0
3720.7	26869		5	16,1	0
3717.5	26892	26896	5	14,0	2
3704.0	26990		4	17,1	−1
3700.9	27013	27027	4	15,0	0
3684.1	27136	27136	3	16,0	0
3667.6	27258	27264	3	17,0	0

Table 2
Vibrational isotopic shift in ZnBr bands

Assignment (v', v'')	Observed Shift in cm^{-1}	Theoretical shift in cm^{-1}
17,0	11	11
16,0	10	10
15,0	10	9
17,1	10	9
14,0	9	8
16,1	9	9
18,2	9	9
13,0	9	10
19,3	8	8
12,0	8	9
11,0	7	7
10,0	7	6

(i) Rotational structure of heavy molecules like the one under investigation could not be resolved under the resolution used.

(ii) Under the moderate dispersion used in the present case the vibrational bands of one sequence may overlap with those of others.

The line-like structure could then be explained by assigning them the appropriate values of (v', v'').

Following the usual procedure (Herzberg, 1950) the vibrational constants of the molecule were determined and the following vibrational quantum formula, which accounts in a satisfactory manner for all the observed bands, was derived.

$$\nu_{head} = 25138.7+[135.80(v'+1/2)-0.40(v'+1/2)^2]$$
$$-[269.80(v''+1/2)-1.54(v''+1/2)^2]$$

As the abundance ratio of the two isotopes of bromine (Br^{79} and Br^{81}) is nearly equal one may expect the intensities of the corresponding isotopic bands to be nearly the same. The isotopic separations for the less abundant molecule $ZnBr^{81}$ have been calculated using the formula :

$$\nu_i - \nu = (\rho-1)[\omega'_e(v'+1/2) - \omega''_e(v''+1/2)] -$$

$$(\rho^2-1)[\omega'_e x'_e(v'+1/2)^2 - \omega''_e x''_e(v''+1/2)^2]$$

Some of the bands for which the isotopic separation is appreciable have been shown in table 2. The isotopic separations for the bands in the longer wave—length region are less than 5 cm^{-1} which may account for the diffuse nature of the bands in that region.

The spectrum of this molecule in the near ultra-violet region has also been studied (Rajan, 1967) and a frequency of about 271 cm^{-1} is obtained for the lower state which is in good agreement with the value obtained in the present investigation.

For the zinc bromide molecule the low lying state belongs to the electronic configuration $\sigma^2\sigma^2\pi^4\sigma$, $^2\Sigma^+$ and in all probability is the ground state. The upper electronic state can not be specified precisely though in all probability the transition may be $\sigma^2\sigma\pi^4\sigma^2$, $^2\Sigma^+ \rightarrow \sigma^2\sigma^2\pi^4\sigma$, $^2\Sigma^+$ (ground), involving a transition of the electron from an inner σ to the outer σ orbit, which is consistent with the observed decrease in the vibrational frequency of the red degraded bands of the system.

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